4-1-2004

Determination of Carbon Nanotube Modification by TG-MS and Pyrolysis-GC/MS

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DETERMINATION OF CARBON NANOTUBE MODIFICATION BY TG-MS AND PYROLYSIS-GC/MS

A Thesis
Presented to
The Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
Of the Requirements for the Degree
Master of Science

By
Quentin Lineberry

April 2004

DETERMINATION OF CARBON NANOTUBE MODIFICATION
BY TG-MS AND PYROLYSIS-GC/MS

Date Recommended 4/21/04

Director of Thesis

Dean of the Graduate College

5/14/04
Date

ACKNOWLEDGEMENTS

I would like to thank Dr. Wei-Ping Pan for his guidance and assistance during my research. Also, the help and guidance of Dr. John Riley and Dr. Thandi Buthelezi have been invaluable to the progress of my education and the construction of this thesis. I would also like to thank the entire Chemistry Department for their instruction and support during my studies. My gratitude also goes to Dr. John W. Connell for his guidance and suggestions on this project. Finally, I would like to thank my family for supporting me in all my endeavors.

Quentin Lineberry

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BY TG-MS AND PYROLYSIS-GC/MS

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Directed by: Wei-Ping Pan, John T. Riley, and Thandi M. Buthelezi

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Uniform dispersion of carbon nanotubes (CNTs) has been one of the major impediments to the full development of the incredible suite of properties offered by CNTs, specifically single-walled carbon nanotubes (SWNTs). However, investigators at NASA Langley and the National Institute of Aerospace Research have recently obtained (SWNTs) that are soluble in select solvents, including THF, DMAc, and ODCB. The SWNTs were exposed to reagents used in cited fullerene modification chemistry in an attempt to produce soluble SWNTs. Upon further examination, it was determined that the intended functionalization had not occurred, and some other phenomenon was responsible for the SWNTs solubility. Determination of what was imparting solubility to the SWNTs was the goal of this project.

The two evolved gas analysis (EGA) techniques used during this project were thermogravimetry-mass spectrometry (TG-MS) and pyrolysis-gas chromatography/mass spectrometry (GC/MS). Samples were heated while the gasses evolved were monitored to determine their identities. The soluble SWNTs were less stable than the non-soluble SWNTS. In addition, they also had much more complicated degradation schemes as

evidenced by the additional mass loss events seen in the TG-MS data. Based on the data, some form of methoxide or methanol is imparting solubility to the SWNTs.

I. INTRODUCTION

A. CNTs

1. Discovery

Carbon nanotubes (CNTs) were first discovered in 1991 by Sumio Iijima.[1] These multi-walled carbon nanotubes (MWNTs), along with other forms of carbon, were found at the negative electrode of an arc discharge setup.[2] In 1993, another type of CNT was discovered by Iijima and Ichihashi--single-walled carbon nanotubes (SWNTs).[3] Iijima was also involved in the synthesis of CNTs with the smallest theoretical diameter possible—0.4 nm.[4] However, another group also reported in the next article of the journal achieving CNTs of the same size, but theirs were primarily SWNTs.[5]

2. SWNTs & MWNTs Properties and Relationship to Fullerene Chemistry

SWNTs can be envisioned as a sheet of graphite rolled up to form a cylinder with there being several different ways to roll up the sheet to produce slightly different SWNTs.[6] CNTs have diameters of around 1 nm and can have open ends or closed ends. Open-end CNTs have primarily six-membered rings because five-membered rings introduce curvature, which leads to closure to close-end CNTs.[7] At their ends, closed-end CNTs are thought to resemble Buckminsterfullerene, where similar curvature is seen.[8] A representation of a SWNT can be seen in Figure 1. MWNTs simply consist of many concentrically aligned SWNTs.

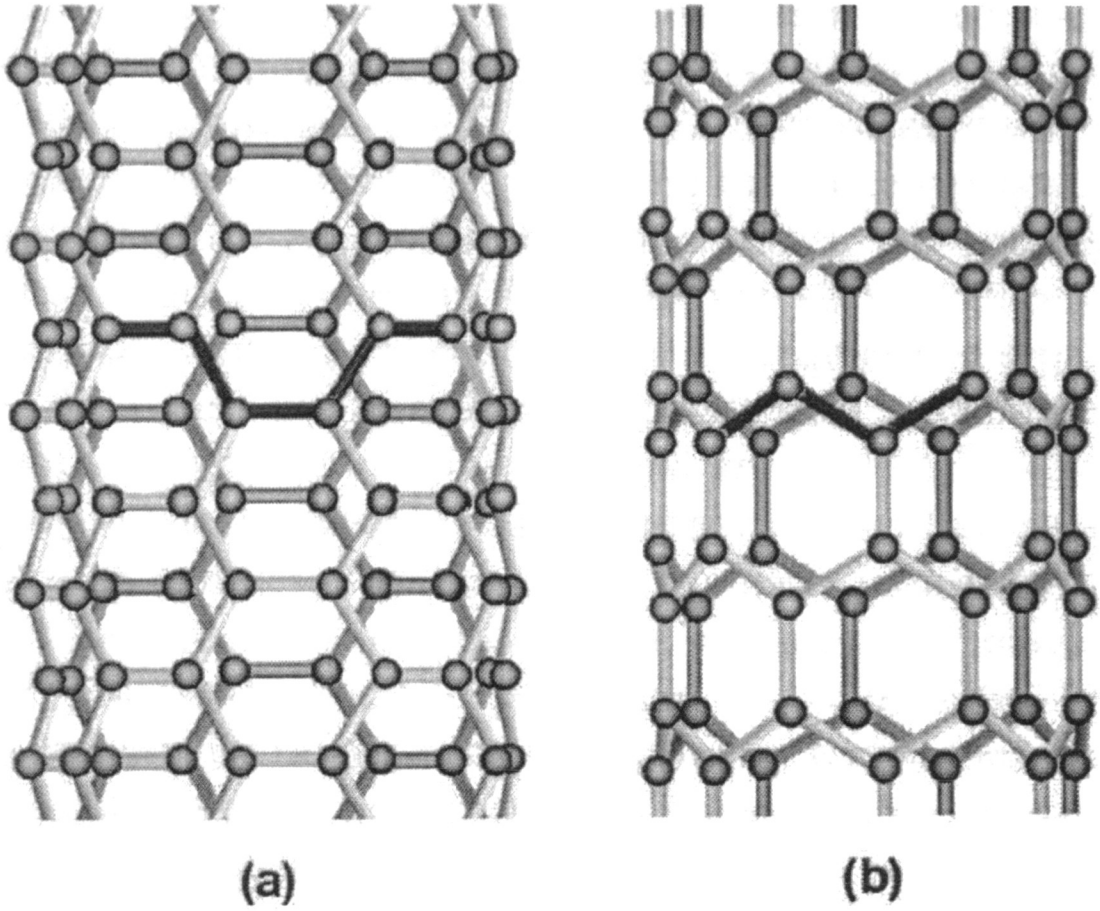

Figure 1. Schematics of arm-chair (a) and zig-zag (b) SWNTs.[9]

3. Methods of Production

A few methods have been tried in order to synthesize CNTs. The most common are arc-discharge, laser ablation, and chemical vapor deposition (CVD). As mentioned earlier, arc-discharge was the first method by which CNTs were observed.[1] The arc-discharge method utilizes carbon electrodes that are placed only a few millimeters apart. A current is then passed between the electrodes causing the carbon to vaporize. Some of the vaporized carbon recondenses to form CNTs, usually SWNTs. However, the addition of transition metals will produce SWNTs. Figure 2 shows a schematic of an arc-discharge setup.

Laser ablation is another common technique used to produce CNTs. A carbon target, typically graphite, is placed in a tube within a furnace purged with an inert gas. The laser is used to vaporize the target, and the purge gas carries the vaporized carbon down the tube where it is collected on a water cooled condenser.[10] Figure 3 shows a schematic of a laser ablation system. As with the arc-discharge method, it appears that addition of transition metals promotes formation of SWNTs over MWNTs.[2]

Both arc-discharge and laser ablation methods have limitations when it comes to scale-up. Both methods use a carbon supply that depletes with time and must be replaced. Also, they require high temperatures, and the lasers for laser ablation are specialized, expensive equipment. The nanotubes retrieved from both methods are tangled and in the form of a powder or a porous membrane, which makes purification more difficult.[11, 12]

Chemical vapor deposition (CVD), or thermal decomposition, of hydrocarbons has shown some promise for large-scale production of nanotubes. Instead of using a

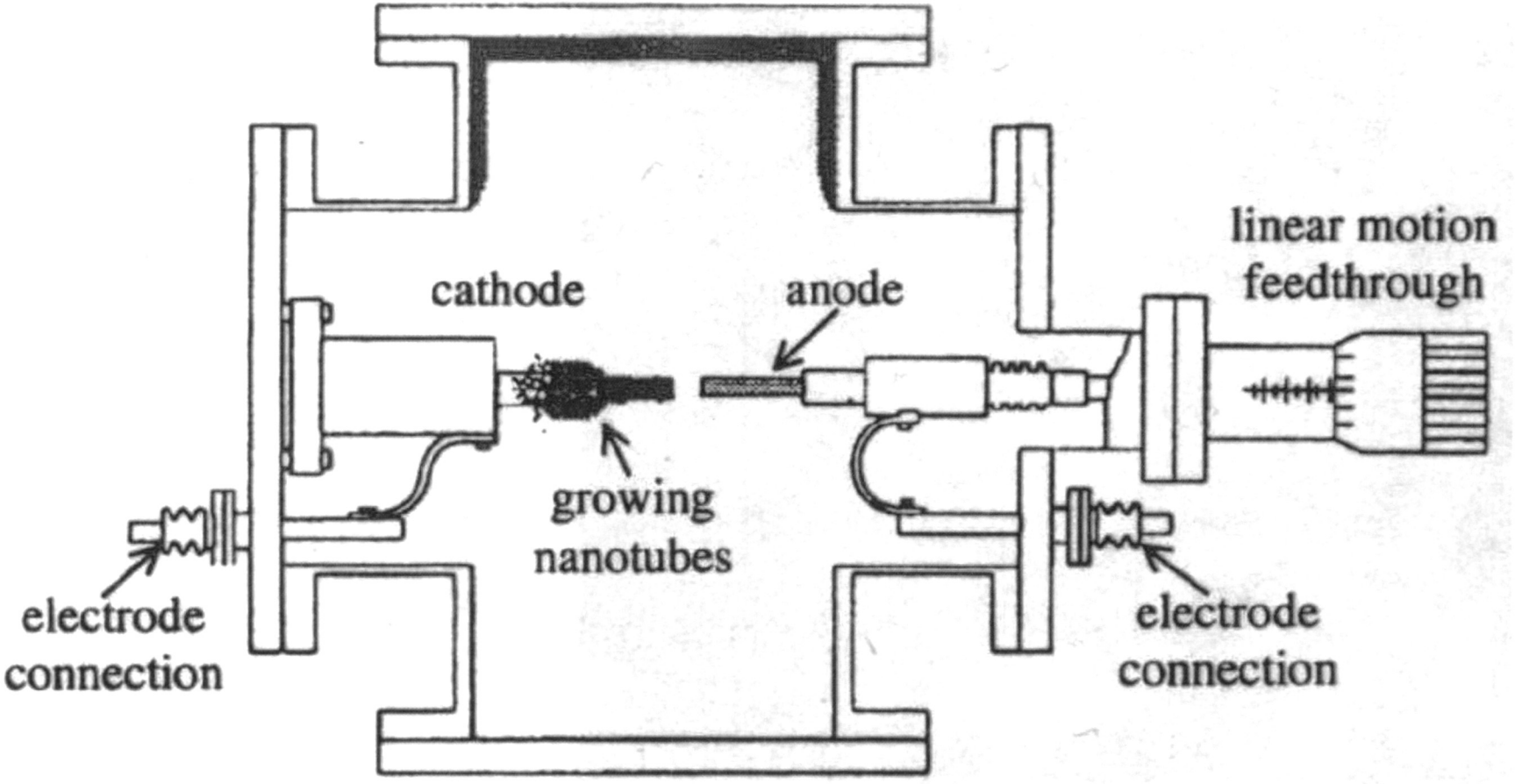

Figure 2. Schematic of arc-discharge setup.[13]

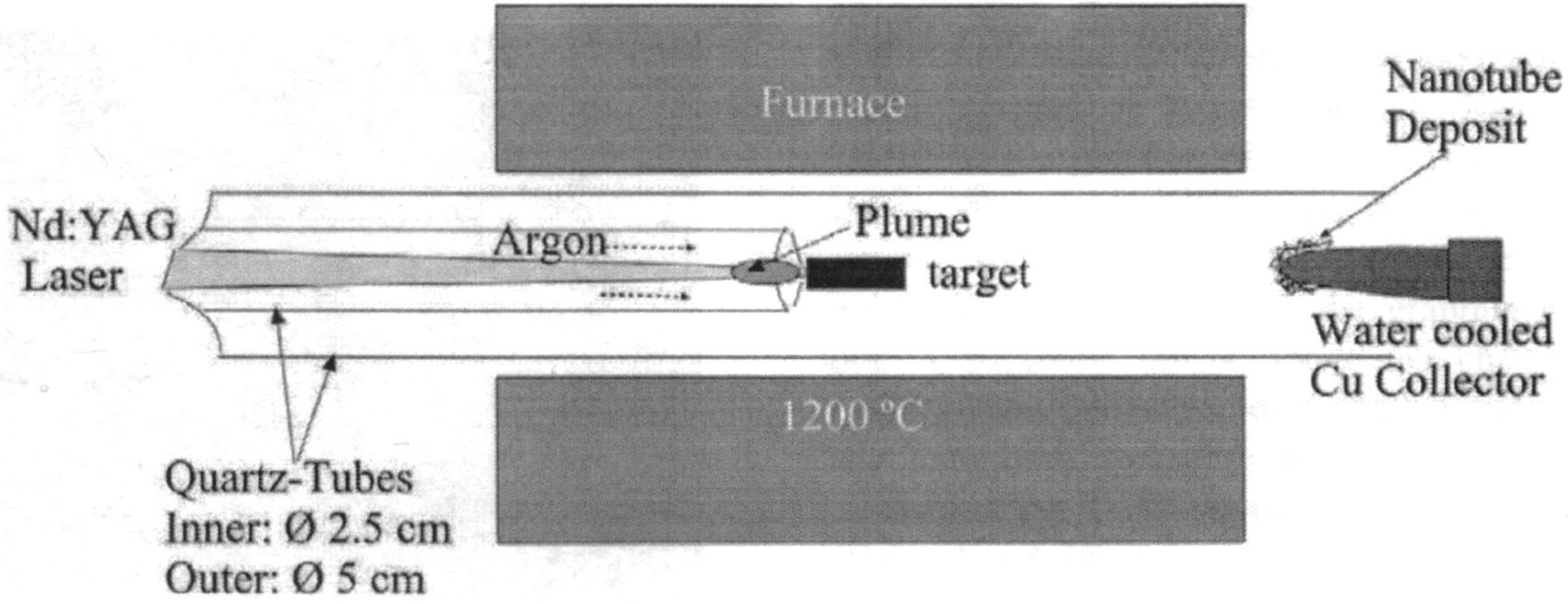

Figure 3. Schematic of laser ablation system.[10]

solid target or electrode, CVD utilizes a flowing stream of hydrocarbon/N_2 gas through a quartz tube in a furnace. The hydrocarbon, typically ethylene or acetylene, decomposes and deposits itself onto a substrate. Figure 4 shows a schematic of a CVD system. Addition of metal catalyst, whether in the gas stream or in the catalyst, promotes formation of SWNTs. Obviously metals, play a key role in the formation of SWNTs, since they enhance their formation in all three methods discussed; however, they also contaminate the as-produced CNTs.

A variation of CVD is the high pressure CO disproportionation (HiPco) process developed by Richard Smalley and coworkers. The process uses CO as the carbon source and $Fe(CO)_5$ as the catalyst. The catalyst is injected into a stream of flowing CO inside a furnace under high temperature and pressure. A schematic of this setup can be seen in Figure 5. SWNTs can be produced with this method that are free of amorphous carbon. This process has even been commercialized by Carbon Nanotechnologies, Inc. for production of SWNTs.[9]

CNTs growth is believed to be a two-step process.[14] The first step is formation of carbon rods followed by graphitization of these rods. Graphitization can start anywhere along the length of the rod with the hollow segments eventually connecting; however, usually graphitization begins at one or both of the ends.

4. Purification

Due to the impurities present from any of these techniques, whether they be the metal catalyst (Fe, Co, and/or Ni) or other forms of carbon (buckyballs or the carbon shell encasing the metal), some type of purification needs to be performed to obtain

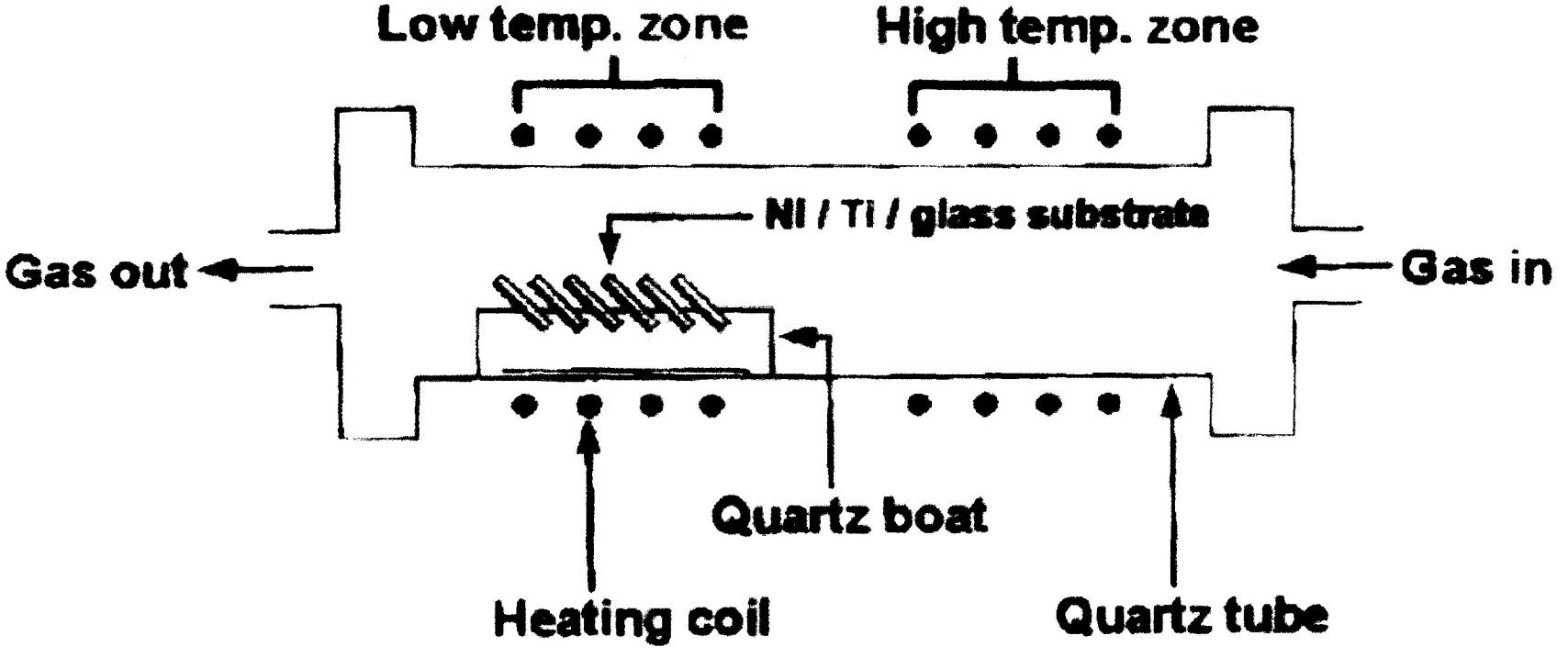

Figure 4. Schematic of CVD system with dual temperature zones.[16]

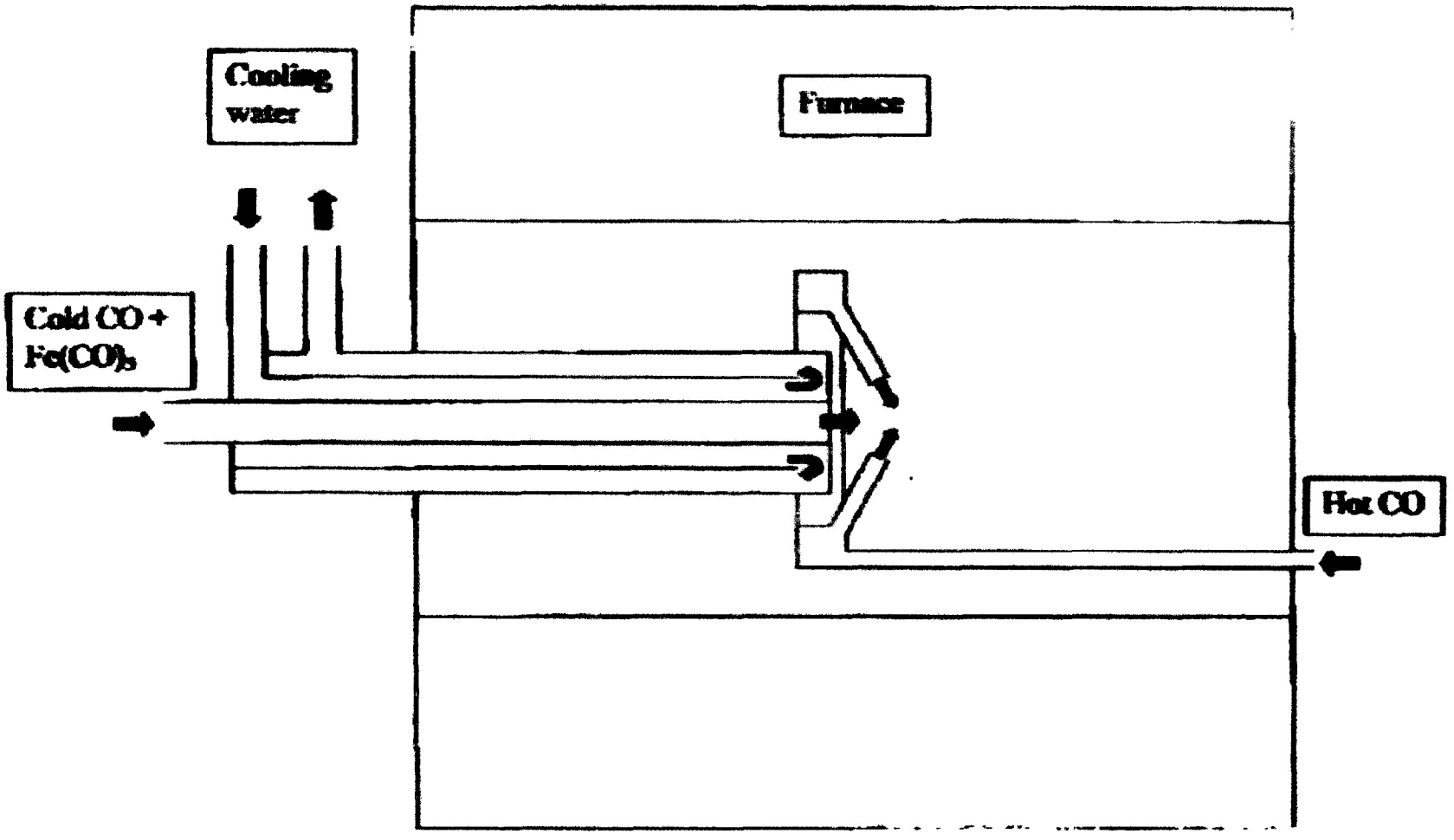

Figure 5. Schematic of HiPco setup. [17]

isolated nanotubes.[15] The purity of nanotubes is usually expressed as a weight ratio of the CNTs to the metal or to other forms of carbon. Several purification techniques have been attempted, including filtration, chromatography, centrifugation, and oxidation (gas or acid).[18,19] There have been variations on these techniques, with one of the more promising being developed by Smalley and coworkers for their HiPco generated SWNTs, which contain enough iron after synthesis to ignite when exposed to a camera flash.[20,21] By using TGA, Smalley and coworkers were able to monitor the weight gain due to oxidation of the metal followed by the weight loss due to loss of carbon. Based on this study, they were able to optimize conditions for the purification of their HiPco SWNTs. A wet O_2/Ar mixture, or air, is passed over the sample in a furnace heated to at least 225°C for 18 hours followed by sonication in HCl to remove the metal oxides.

5. Techniques to Disperse CNTs

One of the current drawbacks to the wide spread use of CNTs is their inability to be evenly dispersed either in a polymer matrix or in a solvent. Several groups have attempted to overcome this problem by a variety of means, including covalent modification,[22] non-covalent modification,[23] and sonication.[24] Covalent modification involves the addition of compounds to the surface of the CNT, usually via carboxylic acid groups introduced during purification. Noncovalent modifications use the same carboxylic acid groups, but they use an ionic interaction between the carboxyl group and usually the amino group of a surfactant.

6. Applications

A number of applications have been envisioned for CNTs since their discovery. They could be used for gas storage media, electronics, AFM tips, solar collectors, and

reinforcement for nanocomposite materials.[25, 26, 27] Reinforcement of polymers has the potential to open a door to entirely new materials. As reinforcing agents, CNTs not only add strength but they can also impart electrical conductivity, which in the case of aerospace applications would allow the material to mitigate electrostatic charge build up.

B. Gossamer spacecraft

Gossamer is defined as "a film of cobwebs floating in air in calm clear weather" or as "something light, delicate, or insubstantial."[28] The second definition is more closely related to the term NASA uses to describe certain space vehicles. Gossamer spacecraft are large, deployable, lightweight pieces of equipment that can be packaged into a very small space and then somehow deployed (typically by inflation) once in space. The unique packaging and deployment requirements for Gossamer spacecraft materials dictates that they be robust, flexible, and space durable.[29, 30] Some applications also require electrical conductivity, optical transparency, or low solar absorptivity. Gossamer spacecraft have been envisioned for uses such as large telescopes, solar concentrators, radio antennas, and solar sails. The telescopes will hopefully be 20 times bigger than the Hubble Space Telescope while being 100 times lighter.[30] The potential applications for Gossamer technology could be the means behind our first excursions outside the solar system.

C. Purpose

Investigators at NASA Langley and the National Institute of Aerospace Research have obtained CNT samples that are soluble in select solvents. Following cited fullerene chemistry, the CNTs were reacted to produce soluble CNTs. Upon further examination, it was determined that the intended functionalization had not occurred, and some other

phenomenon was responsible for the CNTs solubility. Determination of what was imparting solubility to the CNTs was the goal of this project.

II. EXPERIMENTAL

A. Materials

HiPco SWNTs were purchased from Carbon Nanotechnologies, Inc. They were purified by heating at 250°C for 16 hours in a high humidity chamber followed by Soxhlet extraction in hydrochloric acid (~22.2 weight %) for 24 hours. Pyridine and sodium methoxide (NaOMe) were purchased from Aldrich Chemical Company and used as-received. Methanol and 1, 2-dichlorobenzene (ODCB) were obtained in reagent grade from Aldrich and used as-received.

B. Modification procedure (4 samples)

Sample A was the neat SWNTs. Sample C was sonicated for 3 hours in ODCB followed by heating to 80°C for 16 hours. The SWNTs were then washed three times in methanol and collected via centrifugation. The collected pellet was then dried under vacuum at 100°C for 3 hours. Sample D was sonicated for 3 hours in pyridine followed by addition of NaOMe. The mixture was heated to 80°C for 16 hours while stirring in a nitrogen atmosphere, and then heated to reflux for 3 hours. The pyridine was removed by distillation followed by collection of the nanotubes via centrifugation. The centrifuged pellet was washed three times with methanol and dried under vacuum at 100°C. Sample E was prepared by sonicating 100 mg of SWNTs and 220 mL ODCB in a 250 mL round-bottom flask in a water bath for 3 hours. In a separate flask, 0.264 g NaOMe and 80 mL pyridine were stirred vigorously. The SWNT/ODCB mixture was then added to the

pyridine/NaOMe solution drop wise. The mixture was heated to 80°C for 16 hours while stirring in a nitrogen atmosphere, then heated to reflux for 3 hours. The pyridine was removed by distillation followed by collection of the nanotubes via centrifugation. The centrifuged pellet was washed three times with methanol and dried under vacuum at 100°C. There was a sample B, but not enough was received to conduct testing. The experimental conditions are summarized in Table 1.

Table 1. Summary of Experimental Reagents.

Sample	Sonicated for 3 hours in:	Heated for 16 hours in:
CNT A	N/A	N/A
CNT C	ODCB	ODCB
CNT D	pyridine	pyridine / NaOMe
CNT E	ODCB	ODCB / pyridine / NaOMe

C. TG-MS

The combined technique of thermogravimetric analysis-mass spectrometry (TG-MS) provides a powerful tool for the elucidation of compounds evolved during a given mass loss event. By sampling a small portion of the thermogravimetric analyzer (TGA) off-gas, time-resolved mass spectra can be produced for each mass. For example, off-gas analysis allows the user to see if water (m/z = 18) is evolved from a sample. If so, then this evolution of water can be related back to the mass loss event and corresponding temperature on the TGA. However, some species share the same mass-to-charge ratio (m/z), and cannot be distinguished from the MS data alone.

The TG/MS system consists of a TA2960 TGA/DTA (TA Instruments, New Castle, DE) interfaced with a Fisons VG Thermolab Mass Spectrometer (VG Gas

Analysis Systems, Cheshire, England) using a heated capillary transfer line. A schematic of the system can be seen in Figure 6. The sample is heated from ambient temperature to the desired temperature, under a flowing purge gas of either nitrogen or air at 50 mL/min. The capillary transfer line was heated to 170°C, and the inlet port of the mass spectrometer was heated to 150°C. The capillary inlet (1.8 m) is constructed from fused silica encased within a stainless steel sheath and further covered with PTFE and a red fiberglass sheathing. The probe is made of alumina ceramic. This construction allows for good mechanical strength and the means to resistively heat the long capillary line. The Fisons unit is based on the quadrupole design with a 1-300 amu detection range. Detection is accomplished with dual detectors—Faraday cup and Secondary Electron Multiplier. The introduced sample gas is ionized at 70 eV. The system is operated at a pressure of 1×10^{-6} torr.

D. Pyrolysis-GC/MS

Pyrolysis-GC/MS allows for a more definitive identity determination to be made. However, unlike TG-MS, relating a certain species to a specific mass loss event is not as straightforward. Pyrolysis-GC/MS works by cryogenically trapping all compounds evolved over a given temperature range and then introducing all the trapped compounds to the GC as one small sample plug by rapidly heating the cryogenic focusing system. Beyond sample introduction, the technique behaves just like a standard GC-MS experiment with the compounds being separated by the GC and then identified using the MS. A given species can be related to a given mass loss event only if the sample is pyrolyzed over one mass loss event.

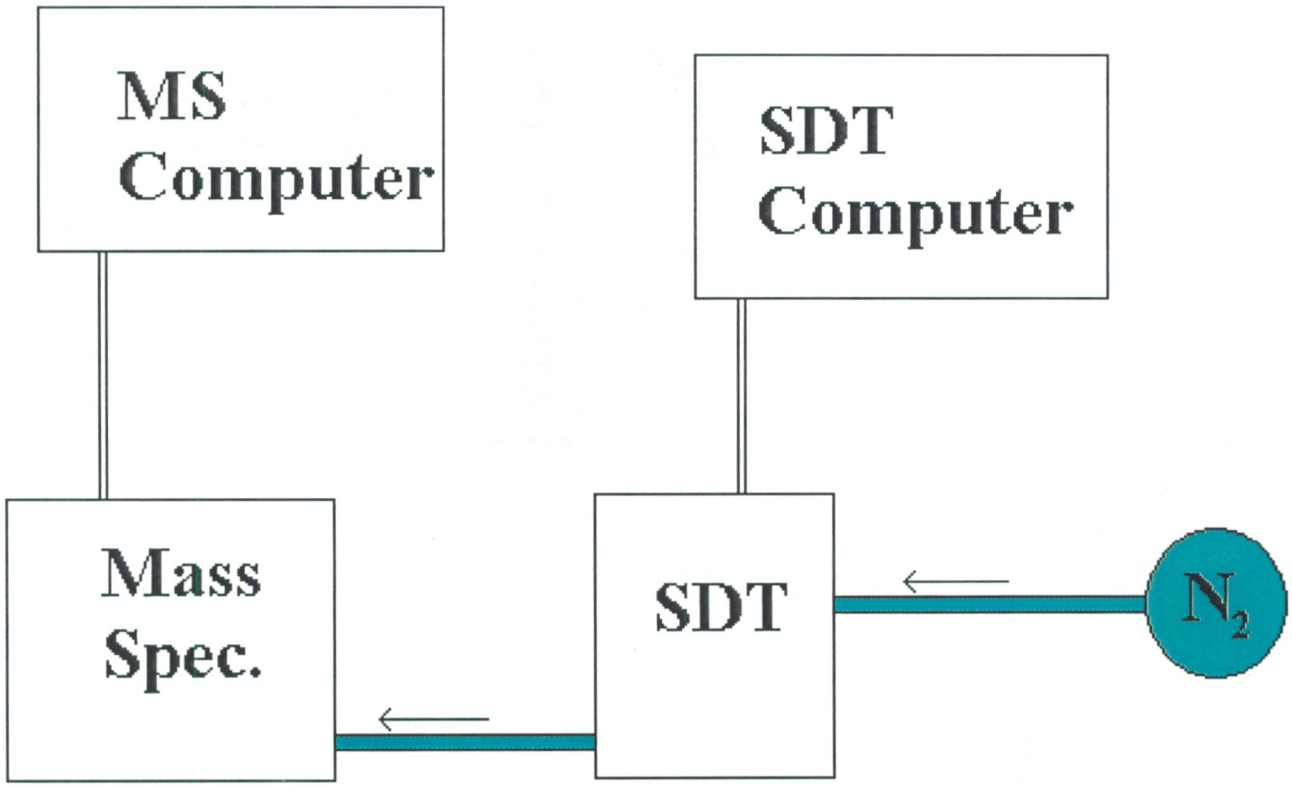

Figure 6. Schematic of the SDT-MS setup.

The Pyrolysis/GC-MS system consists of a LECO® ThermEx™ Inlet System, a LECO® Pegasus® II GC/MS system (LECO Corporation, St. Joseph, MI), and a Smart Cryo™ Smart Cryogenic Focusing Device (HISI Analytical Technologies, Humble, TX). The Pegasus® II GC/MS system includes a HP 6890 High Speed Gas Chromatograph (Agilent Technologies, Palo Alto, CA) and a time-of-flight (TOF) mass spectrometer (LECO Corporation, St. Joseph, MI). A schematic of the setup can be seen in Figure 7. The advantage of TOF mass spectrometry is its potential for tremendously fast acquisition rates. The ThermEx™ Inlet System is designed to heat small quantities of a sample in a quartz pyrocell and transfer the volatilized sample components to a heated capillary GC injection port. The carrier gas connections and seals have been designed to provide a leak-free system for operation with GC-MS system. The associated GC has a capillary injector capable of operating in the split mode and an oven configured with a cryogenic option (liquid nitrogen). During the sample heating period, evolved volatiles are condensed at the column head by maintaining the GC oven at cryogenic temperature. Once the sample has been heated to the desired temperature in the ThermEx™ system and all out-gassed components condensed at the column head, the cryogenic system is very rapidly heated to vaporize the components and inject them into the GC column for analysis. The GC capillary column used was HP-5 with a size of 30 m x 0.32 mm x 0.25 μm. The GC oven program was set as follows: ramp from 50°C to 300°C with a heating rate of 50°C/min. The injection temperature was 295°C.

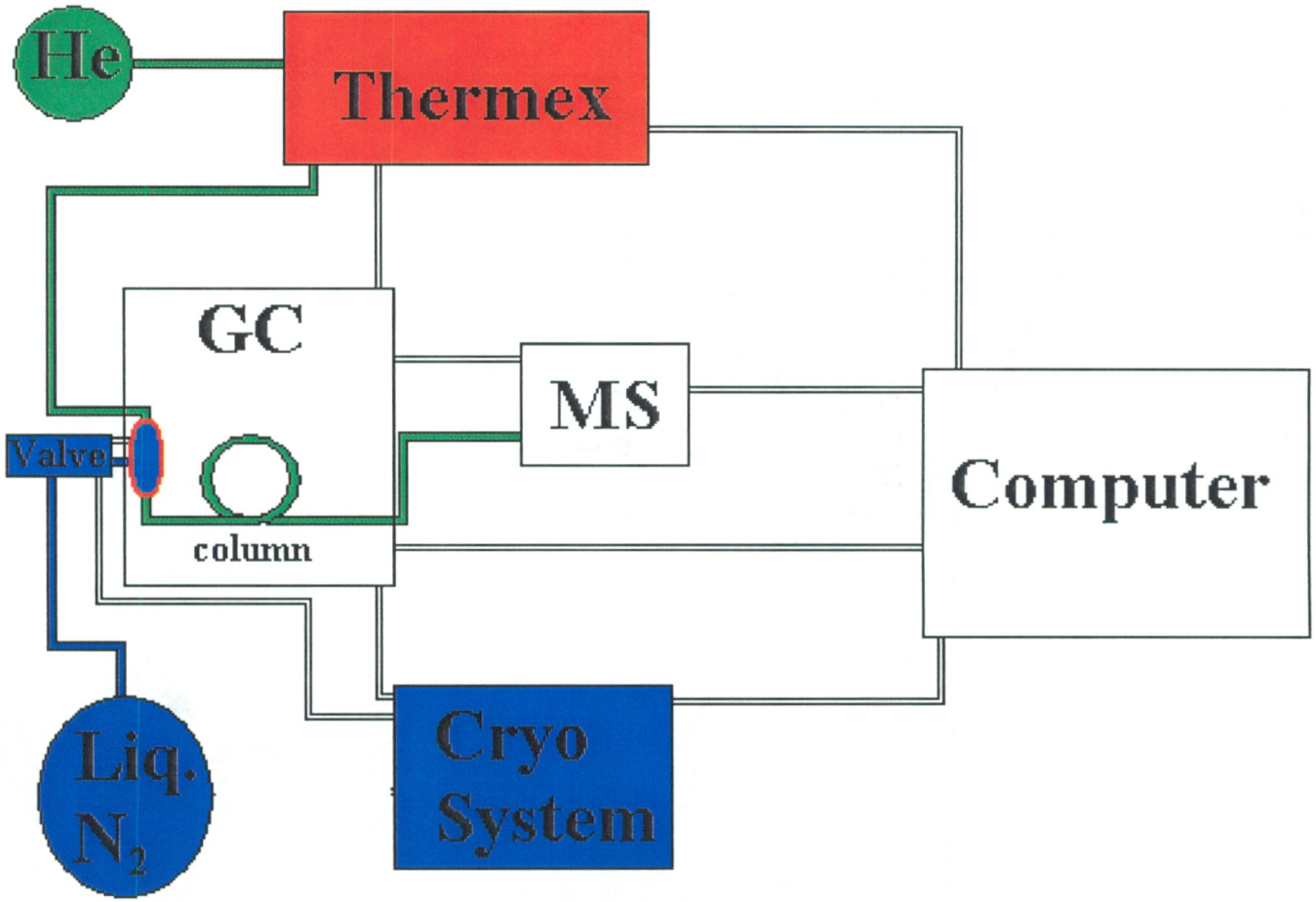

Figure 7. Schematic of the pyrolysis-GC/MS system.

III. RESULTS & DISCUSSION

A. TGA

CNT A and Cs derivative thermogravimetry (DTG) curves show essentially four mass loss events as can be seen in Table 2 and Figure 8. CNT C loses nearly three times as much mass during the second mass loss event, while CNT A loses slightly more during the high temperature event. The difference in residues remaining at the end of the heating program is roughly equivalent to the difference in mass loss during the second mass loss event, possibly implying absorption of a reagent.

The soluble samples, CNTs D and E, have slightly more complicated, but similar, DTG curves showing at least nine distinguishable peaks each, as can be seen in Figure 9. CNT Ds DTG differs from CNT Es due to the addition of a peak at 410°C, and the shifting of the high temperature peak by roughly 100°C.

Figure 10 shows the TGA curves for the four samples. Initially, the soluble samples, D and E, are more thermally stable in the 200-300°C range. This level is too high a temperature to be attributed to water loss. After 300°C, CNTs D and E begin to decompose faster, as indicated by the slope of their curves. CNT C has a large initial mass loss at around 200°C, after which, it follows the slope and curvature of CNT A very well. CNT C's TGA plot crosses that of the soluble samples in the 650-750°C range. CNT A appears to be the most stable sample given its smaller weight loss over the temperature range examined According to the same logic, CNT E is the least stable since it has the smallest residue remaining at the end of the heating. The soluble samples

Table 2. CNT mass loss events and associated species evolution in nitrogen atmosphere.

CNT	Mass Loss Event	Event Temp (°C)	m/z Ratios Detected										
A	1	64	18										
	2	170	15	37	38	39	41	42	43	50	51	52	54
			55	56	57	58	68	71	84	85	87		
	3	541	78										
	4	863	12	16	22	43	44	46					
C	1	65	18										
	2	180	25	35	36	37	38	47	48	49	51	54	55
			56	57	60	61	63	71	72	73	74	75	76
			83	84	85	86	87	96	97	108	110	111	112
			113	114	146	147	148	149	150				
	3	535	41	51	55	56	57	77	78	91	112		
	4	874	2	12	22	25	44						
D	1	68	18										
	2	130	16	43	44								
	3	261											
	4	410	41	42	43	66							
	5	507											
	6	545											
	7	638											
	8	666	43	44	1	41	42						
	9	1008											
E	1	68	18										
	2	125	22	44	16	12							
	3	209											
	4	263	73	74	75	111	113	146	148	49	50	51	73
			74	75	35	36							
	5	487											
	6	504	78	56	57	26	41	42					
	7	537											
	8	559											
	9	664	26	22	45	230	2	44	12				
	10	899											
	11	999											

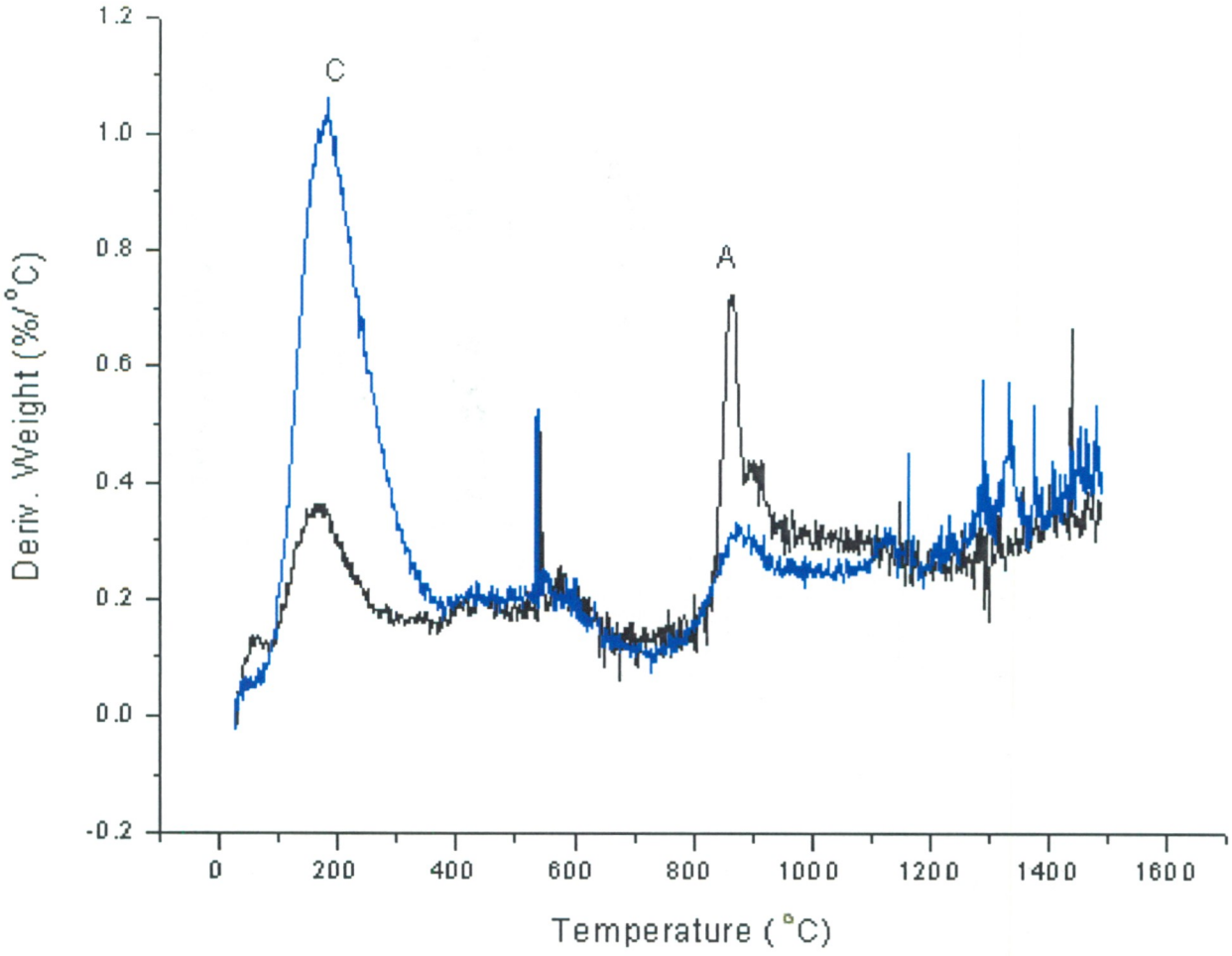

Figure 8. Derivative thermograms of CNTs A and C.

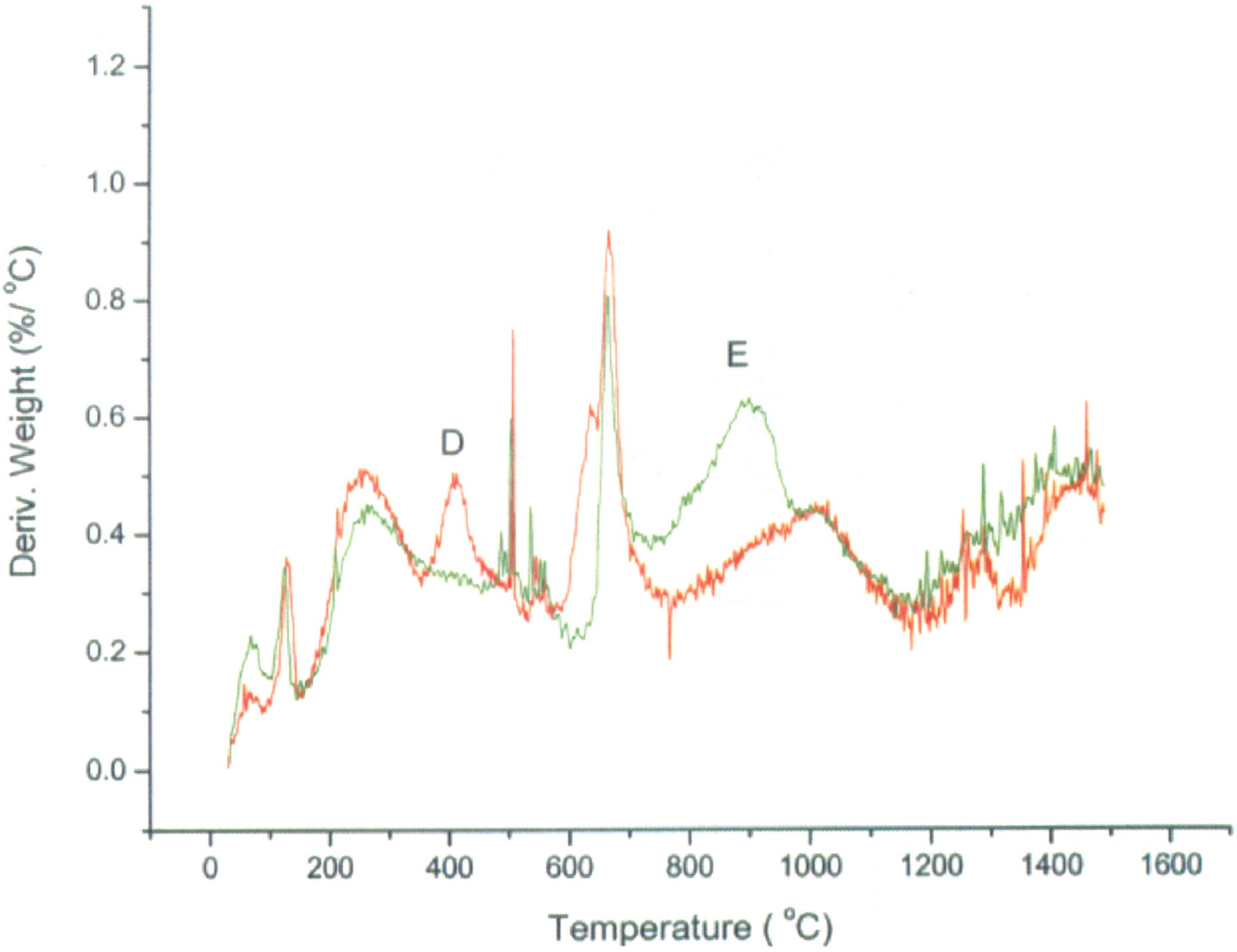

Figure 9. Derivative thermograms of CNTs D &

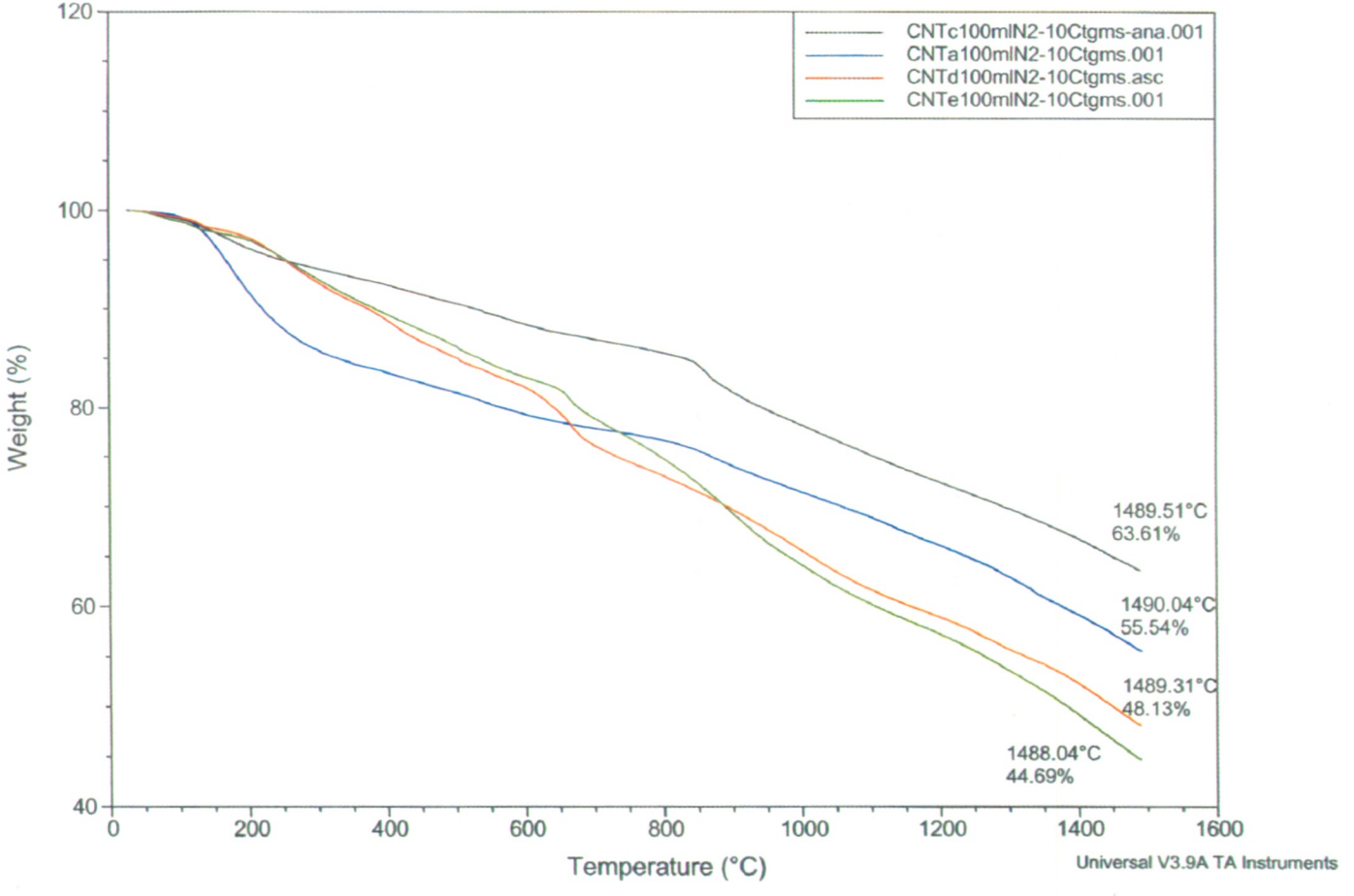

Figure 10. TGA plots of CNTs A, C, D, and E.

are definitely less stable. Closer examination of the MS data may help to prove the assignments of most and least stable sample.

B. TG-MS

A good way to follow the degradation of organic compounds with MS is to monitor the evolution of CO_2 (m/z=44). Figure 11 shows the evolution of mass 44 from the various CNTs in a nitrogen atmosphere. As can be seen from this figure, samples A and C have peak CO_2 evolution at 885°C and 874°C, respectively. Samples D and E have peak evolution at 684°C and 689°C, respectively. Based on these results and the TGA results, CNT A is the most stable. However, according to evolution of CO_2, CNT D is the least stable. This outcome is contradictory to the TGA residue results which found CNT E to be the least stable. Since CNT E had absorbed ODCB during the reaction process, its weight loss seemed exaggerated. Therefore, the SWNT of sample D is the least stable.

Table 2 lists the number of mass loss events, the temperature of each event, and the masses detected related to each event. Some events appear to have no masses detected. There could be several explanations for this lack of detection. The time necessary to take a mass spectrum may be longer than the time scale of the event, such as the sharp spikes seen in the DTG. Also, overlapping of nearby peaks obscures some minor evolutions.

Certain species, such as the solvents and reactants used, can be expected in the MS results. Dichlorobenzene appears in samples C and E, but not in samples A and D, since it was not used. Evolution of the top four masses for dichlorobenzene from sample C, as based on the the NIST webbook, can be seen in Figure 12. Dichlorobenzene

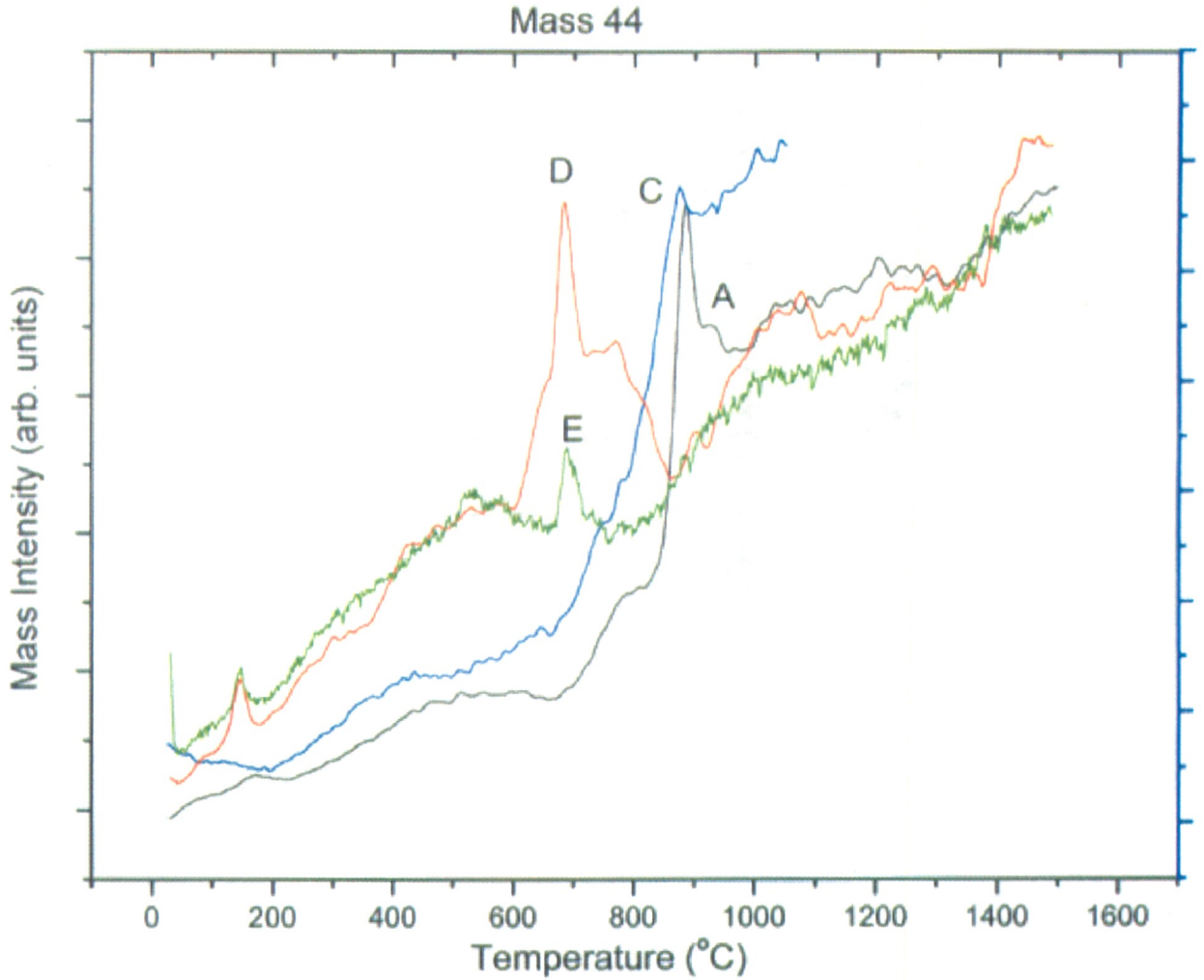

Figure 11. Evolution of m/z = 44 as a function of temperature from all samples.

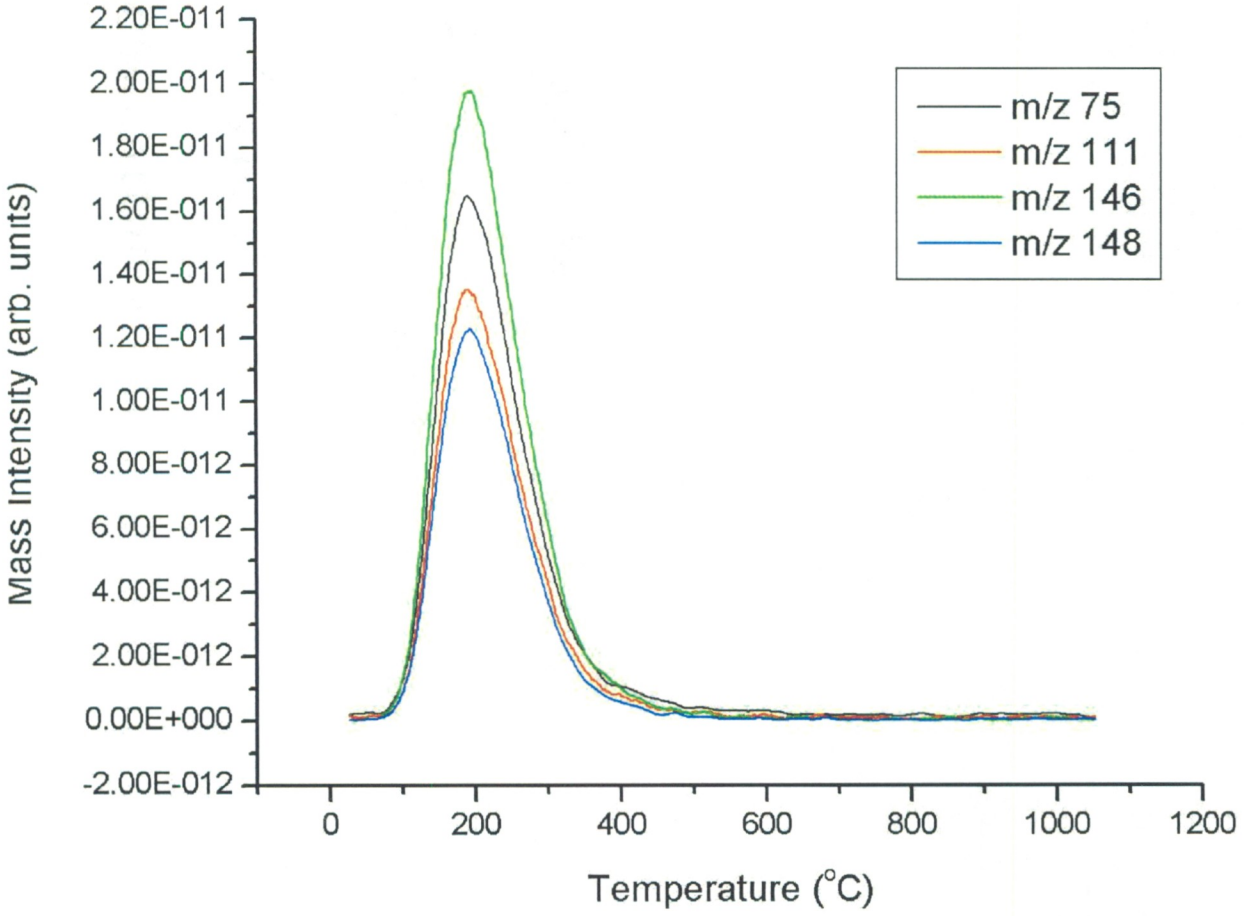

Figure 12. Evolution of dichlorobenzene from sample C.

evolves during the first mass loss event after the initial water loss from about 100°C to 400°C. Evolution of dichlorobenzene causes the 2nd mass loss event of CNT C to be so much bigger than that of CNT A. Given that the evolution of carbon species from CNTs A and C are almost identical, the only difference between the two is that CNT C absorbed some of the solvent, dichlorobenzene.

Pyridine could also be expected in some of the samples, namely D and E. Evolution of this species can be seen, but the peak is not as well defined as the dichlorobenzene peaks discussed earlier. Also, evolution of pyridine occurs at a higher temperature than that of dichlorobenzene from around 200°C to 700°C.

Although CNTs D and E have somewhat similar DTGs, it appears their evolution of species differs substantially. We intend to repeat the CNT D in nitrogen experiment to confirm the current results. CNT E shows a spike around 600 °C of m/z = 230.

Figures 13-16 show the evolution of methanol masses from the four samples. As can be seen from Figures 13 and 14, samples A and C had little to no evolution of anything related to methanol. On the other hand, Figures 15 and 16 show that CNTs D and E evolved many of the masses related to methanol. This evolution occurs over a wide temperature range from the initial temperature to around 900°C, which is unusual given the normally more well-defined evolution seen in TG-MS. On this basis, some form of methanol, in a range of localized environments, could be imparting the solubility to the SWNTs.

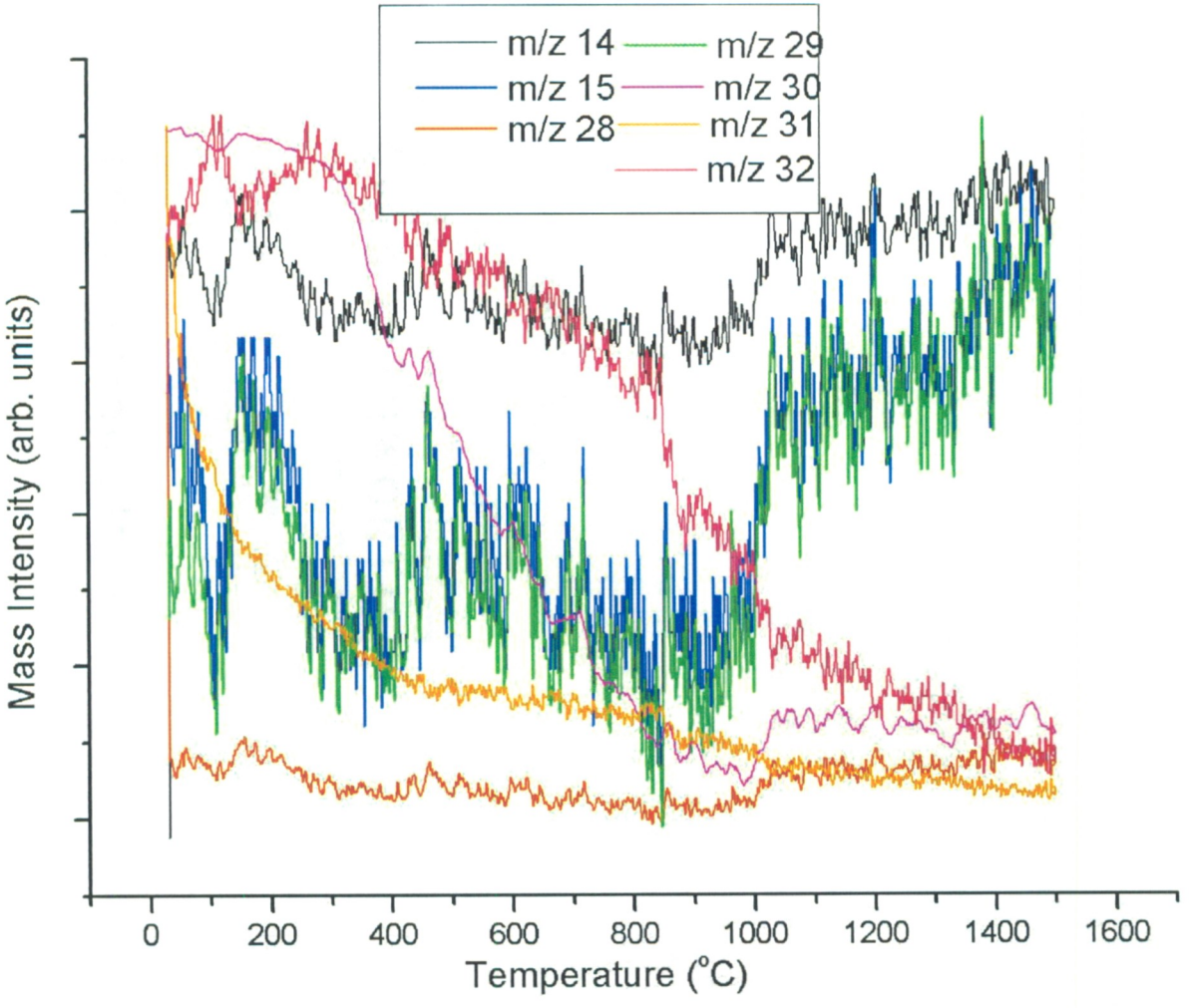

Figure 13. Evolution of methanol masses from sample A.

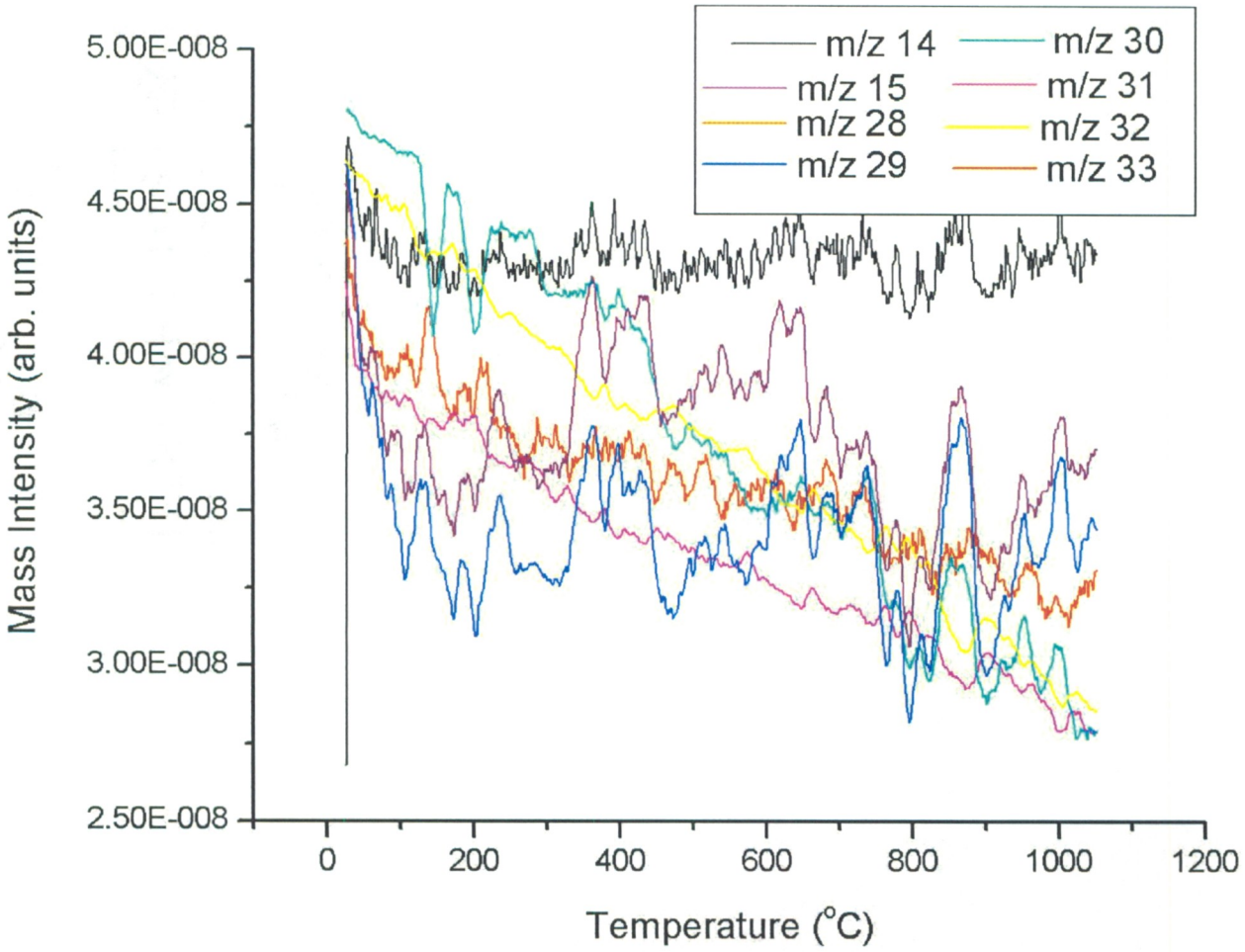

Figure 14. Evolution of methanol masses from sample C.

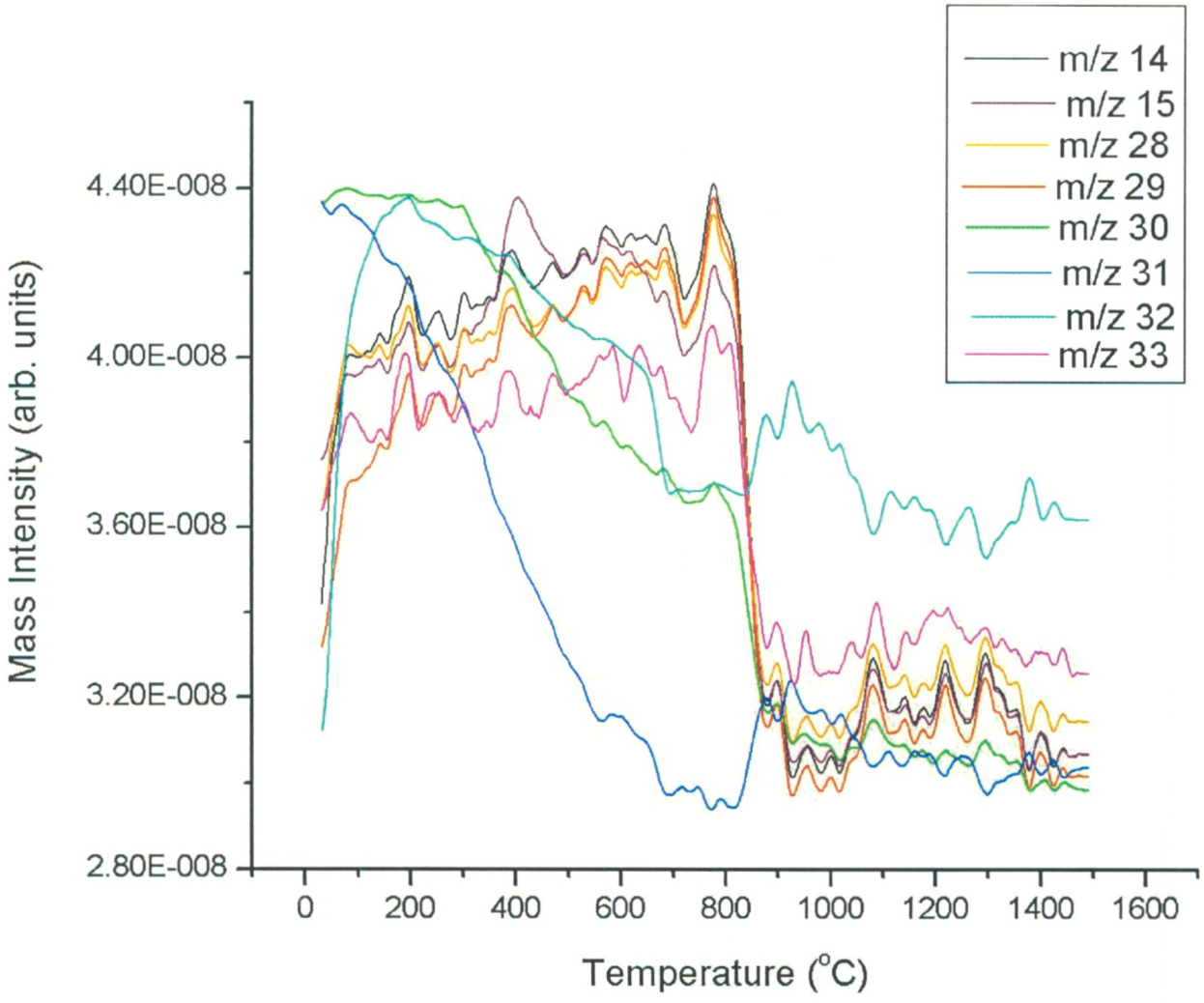

Figure 15. Evolution of methanol masses from sample D.

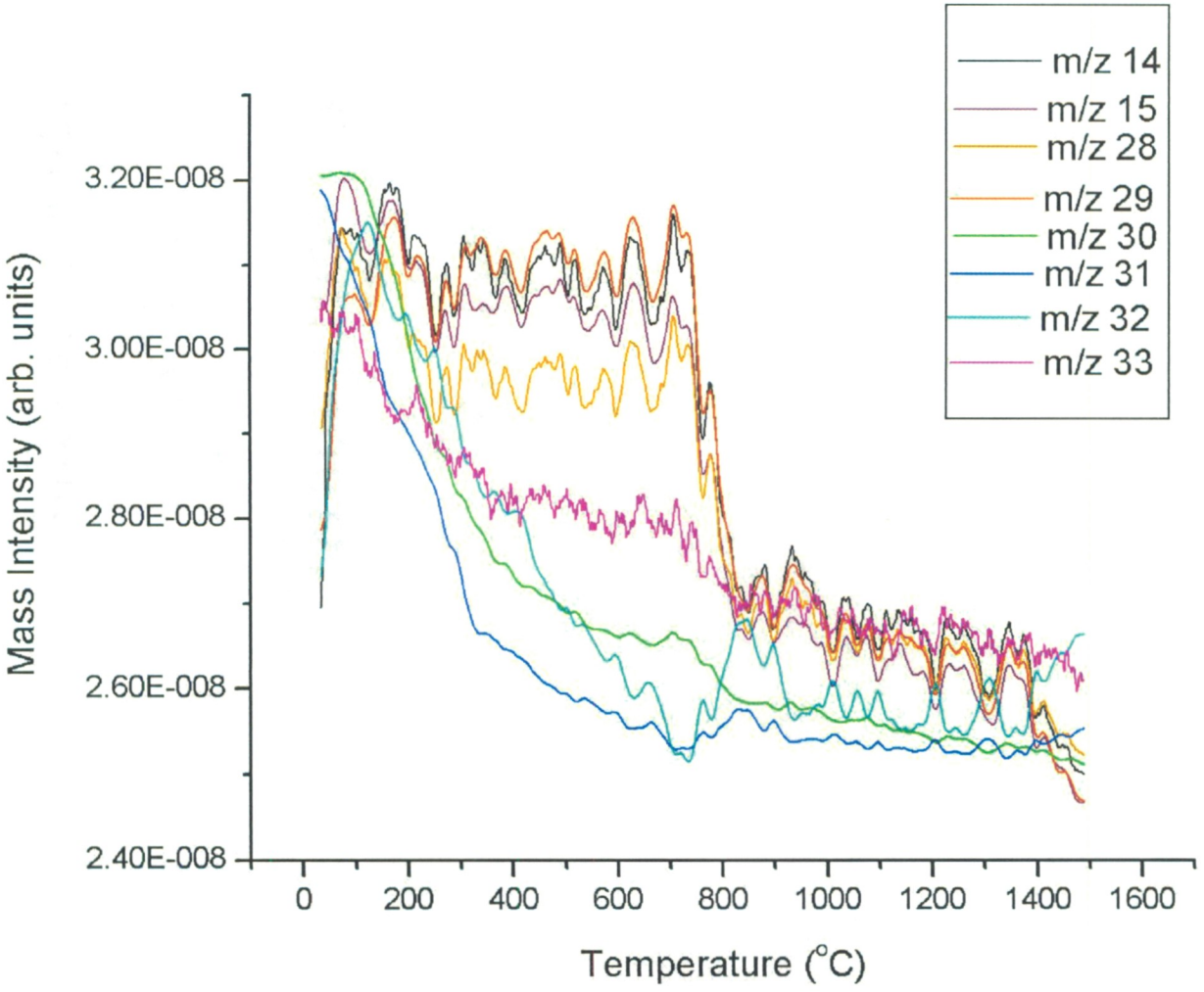

Figure 16. Evolution of methanol masses from sample E.

C. Pyrolysis-GC/MS

Pyrolysis-GC/MS experiments were performed in a helium atmosphere. Each pyrolysis-GC/MS experiment was divided into two segments—one from 50°C to around 200°C and another from 200°C to 700°C. The upper and lower limits of these ranges correspond to the operating range of the instrument.

There are several compounds identified with the MS NIST database that all of the CNT samples produce—benzene, toluene, ethylbenzene, p-xylene, 1,2,3-trimethyl benzene, 1-ethyl,3-methyl benzene, naphthalene, and biphenyl. The compounds can be assumed to be a result of decomposition of SWNTs in general. The presence of benzene and it's derivatives in the evolved gas is expected given that the starting material is a rolled graphite sheet.

However, the following compounds evolved only from the soluble samples, D and E: methanol, pyridine, methyl pyridines, phenol, 1, 3-cyclohexadiene, 2-ethyl hexanal, and cis-a-methylstyrene. Pyridine should be expected in the soluble samples, given the reactants used for the functionalization. The phenol detected here could be the m/z of 94 seen in the TG-MS of sample D. The concentration in sample E could be low enough that the MS was unable to distinguish it from the background. The other compounds could be a result of unforeseen degradation schemes involving both the SWNTs and the substituent providing solubility. The detection of these compounds in addition to the ones found by TG-MS is indicative only of the increased sensitivity of the GC-MS compared to the TG-MS.

Just as with the TG-MS results, the pyrolysis-GC/MS results indicate that methanol is one of the compounds evolved only from the soluble samples. This

confirmation lends some credence to the theory posed in the TG-MS section that some form of methanol is the species responsible for imparting solubility to the SWNTs. A "form of methanol" is used because the reactant used was methoxide, but the instruments detect methanol. Methanol was used to wash the samples three times prior to analysis, but this exposure does not explain why methanol was detected only in the soluble samples. Therefore, some reaction with methoxide or methanol must take place prior to washing that is impervious to the washing. The resilience of this modification leads me to believe that the functionalization has a more covalent nature; otherwise, it would have likely been removed by the washing process.

IV. CONCLUSIONS

The following statements can be made regarding this work:

1. CNT A (pristine SWNT) is the most stable compound.
2. CNT D is the least stable with respect to evolution of carbon containing species.
3. When solubility is achieved, the decomposition temperature decreases dramatically, indicating a modification of the CNT.
4. Some form of methanol is believed to be the modification that is imparting solubility.

As a means to better ascertain what phenomenon is imparting solubility to the CNTs, we intend to perform several more experiments. We have the capability to perform in-situ high-temperature X-ray diffraction experiments. CNT studies with XRD will be limited by the amount of sample. Relatively large amounts of a sample are needed to perform these experiments adequately. Hopefully, we will be able to produce enough of each sample during the center stay that XRD will be practical.

In-situ solid phase thermal Infrared (IR) spectroscopy should be used. In-situ IR will allow for determination of changes in functional groups of the sample as it is heated. This study will be complimentary to the Raman spectroscopy study that was already performed on the sample.

High-resolution TGA could prove beneficial in separating all the mass loss events in the soluble CNT samples (D & E). Rather than ramping linearly over the entire

temperature range, Hi-Res TGA heats the sample dynamically slowing the heating rate during each mass loss event.

Scanning Electron Microscopy and Transmission Electron Microscopy will also be performed to study the structure and morphology of the CNTs and their bundles.

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